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㊾改良された生物学的脱窒素方法

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明　細　書

1. 発明の名称

改良された生物学的脱窒素方法

2. 特許請求の範囲

水中の$NO_2^-$および（または）$NO_3^-$を生物学的に$N_2$ガスとして放出する方法において，脱窒素能を有する微生物と鉄フロックとを付着せしめた樹脂に被処理水を接触させることを特徴とする生物学的脱窒素方法。

3. 発明の詳細な説明

本発明は水中の$NO_2^-$および（または）$NO_3^-$を生物学的に除去するにあたり，脱窒素細菌と鉄フロックとを樹脂に付着せしめ，該樹脂に被処理水を接触することにより，効率よく水中の窒素化合物を除去する方法に関するものである。

生物学的脱窒素法の原理は，嫌気的条件下で脱窒素菌を利用し，原水中の$NO_2^-$あるいは$NO_3^-$で表わされる窒素酸化物中の結合状酸素を水素供与体の存在下で呼吸せしめ，該窒素酸化物の窒素を$N_2$にまで還元分解するもので，これを式で表わすと次のようになる。

$$2NO_2 + 6H^+ \rightarrow N_2 + 2H_2O + 2OH^-$$

$$2NO_3^- + 10H^+ \rightarrow N_2 + 4H_2O + 2OH$$

これを利用した従来の代表的な生物学的脱窒素法は，嫌気的条件下において，水素供与体としてメタノール，エタノール，酢酸などの炭素化合物を添加し混合液中の窒素酸化物を還元せしめるものであるが，その際用いられる脱窒菌はスラッジ状態のため，脱窒処理後スラッジと水層とに分離する沈降分離工程を必要とし，更にスラッジ循環が付加されるなどにより，広大な敷地面積が必要となること，さらに水質変動に対する追随性に困難な問題があつた。このため最近では新しい除去方法として塔式固定生物床による脱窒プロセスが開発され，脱窒性能及び設備上有利であるといわれているが，未だ多くの問題が残されている。

塔式生物床による脱窒素方法において用いられる充填材としては粒状活性炭，樹脂製炉材，石炭，石砂，けい藻土などがあるが，最もよく研究されているのは粒状活性炭と樹脂製炉材である。粒状

活性炭は微生物の付着性が非常に良いが，耐久性および価格の面で有利とはいえず，樹脂製炉材の場合は安価であり耐久性の点ですぐれているが，微生物の付着性が一般に活性炭より劣り，従つて高濃度の窒素除去あるいは水質変動に対する安定性に欠ける等の欠点を有する。

この様な背景において本発明者らは，脱窒能力のすぐれた付着生物床処理方法を確立すべく研究をおこなつた結果，脱窒素菌を鉄フロックと共に樹脂担体に付着せしめることにより，付着力のすぐれた生物膜が形成されることを発見し，本発明を完成した。

即ち，本発明は，脱窒素菌を鉄フロックと共に樹脂担体に付着させて，生物床とし，有機炭素源と共に嫌気条件下に被処理水と接触せしめることにより，原水中の $NO_2^-$ あるいは $NO_3^-$ をきわめて効率よく $N_2$ガス迄還元する方法である。

本発明において用いられる微生物担体は安価で耐蝕性に富み，種々の形に成型可能な樹脂製であり，特に発泡成型品は軽量のため取扱いが非常に容易であり，表面積効率がすぐれ，更に表面の凹凸の存在によつて微生物膜が付着しやすいという点で特に好ましい。

樹脂素材としては，塩化ビニル，ポリスチレン，ポリエチレン，ポリウレタン，ABS樹脂などあるがこれらに限定されることなく使用できる。その成型品の形状は，棒状，粒状，板状，パイプ状，網状などいずれも使用し得るが，充填密度，表面積などに富む粒状成型品が比較的適している。また発泡体としては，発泡倍率2〜40，密度0.005〜0.5$g/cm^3$のものが使用される。

かかる担持体に付着させる脱窒菌としては，通常の活性汚泥中に生息している他栄養性通気性嫌気性脱窒菌で，Pseudomonas denitrificans あるいは Micrococcus denitrificans などが用いられる。

本発明に用いられる鉄フロツクは，酸化鉄又は水酸化鉄などの非水溶性鉄化合物フロツクで，被処理水中に直接酸化鉄又は水酸化鉄を加えるか，鉄塩とアルカリ剤を加え被処理水中で鉄フロックを形成してもよい。鉄塩としては，塩化オ一鉄，硫酸オ一鉄などのオ一鉄塩や，塩化オ二鉄，硫酸オ二鉄などのオ二鉄塩が用いられる。また被処理水がアルカリ性の場合にはアルカリ剤の添加を省略することができる。

また，酸化鉄，水酸化鉄または鉄塩添加量は，乾燥脱窒素菌重量に対して10〜50%であれば充分である。

微生物の付着方法としては，鉄塩溶液又は鉄フロツク懸濁液と脱窒素菌の懸濁液を別々に又は適別混合して被処理槽に満たし，処理槽内において樹脂に接触せしめることにより付着生物床とする方法が用いられる。かくして得られた生物−鉄フロツクの付着生物床に，PH6〜8に調整された $NO_2$あるいは $NO_3$含有水を通水する。この時同時に有機炭素源として，例えばメタノールの場合は窒素あたり2〜3倍量を加えて脱窒処理する。また運転中必要に応じて鉄フロツク又は鉄塩とアルカリ剤を原水に添加補給することもできる。原水の処理槽内における接触時間（平均滞留時間）は，原水中の窒素濃度によつて影響をうけ，例えば $NO_2^-$−N または $NO_3^-$−N として100ppm〜200ppmでは，大体80〜120分である。

これは従来のスラツジ方法と比較して単位窒素あたりの接触時間あるいは単位容積あたりの脱窒素能力が数倍も高いものである。

本発明における適用廃水としては，都市下水，食品工場廃水，コークス炉廃水，繊維工場廃水，化学工場廃水，その他硝酸含有廃水などがあり，種々の廃水に広く適用し得る。

以下本発明の実施例をもつてさらに詳しく説明する。

実施例1

直径5%のポリスチレン発泡体（商品名ウツドラツクC，旭ダウ社製，発泡倍率30倍）を図に示す1ℓ容の管に高さ46cmとなる様に充填し，これに塩化オ二鉄20mgを水に溶解して苛性ソーダで中和することによつて生成する水酸化オ二鉄の懸濁液を流入させて発泡体の表面に鉄フロツクを付着させた。さらに活性汚泥（MLSS 2400ppm）

の撹拌均一化された脱窒菌懸濁液50㎖を採取し、塔内に注入後、硝酸ナトリウム0.685g/ℓおよび燐酸オ一カリウム0.019g/ℓを含む人工調整液を2ℓ加え2日間循環し脱窒菌の固定を行なつた。次いで同上の人工調整液の組成からなる原水（窒素濃度113 ppm）と、メタノールを0.36㎖／原水10ℓとなるように連続的に通水した。他方比較として、鉄フロックを付着させない発泡体に脱窒菌を付着させた場合と粒状活性炭に脱窒菌を付着させた場合とに関しても並行的に行ない、それぞれの脱窒率を求めた結果次の表に示すように本発明の方法は高い脱窒率を示した。

3 days (6 hrs contact)　2 weeks (2 hrs contact)

| | 脱窒率（%）→ % N2 | |
|---|---|---|
| | 通水3日目（接触6時間） | 通水2週間（接触2時間） |
| present invention 本発明方法 | 99% | 98% |
| foamed bodies alone 発泡体のみ | 75% | 79% |
| granulate active carbon 粒状活性炭（武田薬品製） | 98% | 97% |

通水温度20℃

実施例2

実施例1と同様に、ABS樹脂（径5㎜の球状）を充填した塔に、予めMLSS 2400ppm の活性汚泥（PH 5.6）50㎖と、塩化才二鉄を500ppmとなるように加えてフロック状とした脱窒菌を全量注入し樹脂に付着させた。次いで、石油化学系廃水の活性汚泥処理水2ℓを加え、塔内液を循環させることによつて付着生物床とした。活性汚泥処理水中には $NO_2^-$−N 12ppm, $NO_3^-$−N 108ppm含まれていたが有機炭素は殆んど含まれていなかつたので、メタノールを窒素あたり2.5倍量加えて成る排水を2日目より連続的に通水したところ、通水期間3週間：接触60分で脱窒率97%を得た。

以上のように本発明の方法によれば、従来のスラツジ接触循環方法に比較して運転管理上、また設置面積の点でもすぐれており、更に担体が樹脂であるため、活性炭等に比較して価格や、素材の使用量の面からみて非常に有利であり、軽量であり取扱い上の面からもすぐれている。さらに脱窒率が非常に高く、それだけ設備がコンパクトになり、高濃度の窒素除去が出来ること、水質変動に対する安定性も高いので水中の窒素除去を有利におこなうことができる。

4. 図面の簡単な説明

図面は実施例に用いた処理塔を示すものである。

1・・・処理塔

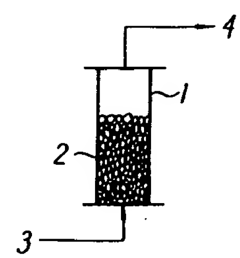
2・・・ポリスチレン発泡体

3・・・被処理水＋メタノール

4・・・処理水

特許出願人　旭化成工業株式会社

図面



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# IMPROVED BIOLOGICAL NITROGEN-REMOVAL METHOD

[CLAIM]

A method for biological extraction as $N_2$ gas of $NO_2$- and/or $NO_3$- in water, characterized in that the water to be treated is brought into contact with a resin wherein microorganisms having a nitrogen-extracting ability and iron flock have caused to be adhered.

[DETAILED DESCRIPTION OF THE INVENTION]

The present invention concerns a method for the removal of nitrogen compounds from within water wherein, in the biological extraction of $NO_2$- and/or $NO_3$- from within water, nitrogen-extracting microorganisms and iron flock are caused to adhere by a resin, and said resin is brought into contact with the water to be treated.

The principle of methods of biological extraction of nitrogen from water is such that nitrogen-extracting bacteria are used under anaerobic conditions so as to cause the bonded oxygen of nitrous oxide compounds, as represented by $NO_2$- or $NO_3$- within the water, to be aspirated in the presence of hydrogen substituents, such that the nitrogen from said nitrogen-containing compounds is reduced and broken down to $N_2$. This can be expressed by the following formulae.

$$2\ NO_2 + 6\ H^+ \dashrightarrow N_2 + 2\ H_2O + 2OH$$

$$2\ NO_2- + 1\ OH^+ \dashrightarrow N_2 + 4\ H_2O + 2OH$$

Prior art representative microorganisms using this mechanism reduce, under anaerobic conditions, the nitrogen compounds within a mixed liquid wherein carbon compounds such as methanol, ethanol, acetic acid, or the like that act as hydrogen substituents have been added; however, the nitrogen-extracting bacteria used are in a sludge state, such that after nitrogen-extraction treatment, a precipitation and separation step wherein the sludge and water layers are separated is required, and there are disadvantages in that large amounts of surface area are required and that it is difficult to keep pace with variations in water quality. Because of this, recently nitrogen-extraction processes using tower-type fixed biological beds have been used as new removal methods. These are said to be advantageous from nitrogen extraction ability and installation standpoints, but many disadvantages still remain.

The filler material used in nitrogen-extraction methods using tower-type biological beds is granulated active carbon, resin filter material, charcoal, sand, diatomaceous earth, or the like, but the most highly researched of these are granulated active carbon and resin filter material. Granulated active carbon has an extremely good adhesiveness for microorganisms, but cannot be called advantageous from

durability and cost standpoints; resin filter material has superior cost and durability, but the adhesive properties with regards to microorganisms are generally worse than that of active carbon, and therefore it has disadvantages with regards to stability in the face of changing water quality or for the removal of high concentrations of nitrogen.

Against this kind of background, the present inventors undertook research to establish a microorganism-adhered treatment method with superior nitrogen-extraction ability, with the result being the discovery that adhering nitrogen-extracting microorganisms together with iron flock within a resin support body forms a biological film with superior adhesive force, and the present invention was completed.

That is to say, the present invention is a method wherein nitrogen-extracting microorganisms are adhered together with iron flock within a resin support body for use as a biological bed, and by bringing water to be treated and an organic carbon source into contact therewith under anerobic conditions, the $NO_2$- or $NO_3$- within the water can be reduced to $N_2$ gas with excellent efficiency.

The microorganism support body used in the present invention is a resin that is low-cost, resistant to corrosion, and capable of molding into various forms; foamed resin products are particularly advantageous in that they are extremely easy to handle because of their light weight, have a surface area with superior efficiency, and

furthermore allow easy adhering of microorganisms due to the presence of surface roughness.

Resin materials include chlorinated vinyls, polystyrenes, polyethylenes, polyurethanes, ABS resins, and the like, but others may be used without being limited to these. As for the shape of the molded product, rods, granules, plates, pipes, webs, and the like may all be used, but a granular molded form is relatively better as it has abundant filler density, surface area and the like. Furthermore, a foamed body having a foaming expansion rate of 2 - 40 and a density of 0.005 - 0.5 g/cm2 is used.

As for the nitrogen-extracting microorganisms to be adhered to the obtained support body, a nitrogen-extracting bacteria that lives within normal sludge and elsewhere and is anaerobic, permeable, and nutritive, such as Pseudomonas denitrificans, Micrococcus denitrificans, or the like can be used.

The iron flock used in the present invention is non-water-soluble ferrous compound such as iron oxide or iron hydroxide or the like; either the iron oxide or iron hydroxide is directly added to the water to be treated, or ferrous salts and alkali agents may be added to the water to be treated such that the iron flock is formed therein. As for iron salts, ferrous salts such as ferrous chloride, ferrous sulfate, or the like, and ferric salts such as ferric chloride, ferric sulfate, or the like can be used. Furthermore, in cases wherein the water to be treated is

alkali, the addition of small amounts of alkali agent is permissible.

Furthermore, an amount to be added of iron oxide, iron hydroxide or ferrous salts of 10 - 50% with regards to the percent by weight of dry nitrogen-extracting microorganisms is sufficient.

As for the adhesion method for the microorganisms, a method wherein a ferrous salt solution or suspended iron flock solution and a suspended solution of nitrogen-extracting organisms are separately or simultaneously mixed and then placed into a treatment tank, and a biological bed is formed by means of bringing this into contact with resin within the treatment tank. Water containing $NO_2$- or $NO_3$- and having a pH adjusted to from 6 - 8 is passed through this obtained biological bed wherein organisms and iron flock have been adhered. An organic carbon source is added at the same time; in the case of methanol, 2 - 3 times by weight per amount of nitrogen is added and nitrogen-extraction processing is undertaken. Furthermore, iron flock and alkali agent may be added to the base water as necessary during the process. The contact time for the base water in the treatment tank (average [illegible] time) is influenced by the nitrogen concentration within the base water, but in an example wherein the $NO_2$-N or $NO_3$-N is from 100ppm - 200ppm, it is generally 30 - 120 minutes.

This has a contact time per unit of nitrogen or nitrogen capability per unit of capacity that is several times greater in comparison to prior art sludge methods.

The present invention can be applied to a wide variety of wastewaters including uurban sewage, food-processing wastewater, coke furnace wastewater, fiber factory wastewater, chemical factory wastewater, and other sulfate-containing wastewaters.

The invention will be explained in further detail via an embodiment.

[EMBODIMENT]

Polystyrene foamed bodies of a diameter of 5mm (product name uddorakku C, Asahi Dow Corp., foaming rate of 30x) were, as shown in the figure, filled within a 1-liter capacity tower to a height of 46cm; a suspended solution of ferric hydroxide formed by dissolving 20mg of ferric chloride in water and neutralized with caustic soda was allowed to flow therein such that iron flock adhered to the surface of the foamed bodies. Furthermore, after injecting 50ml of a nitrogen-extracting bacteria suspension wherein active sludge (MLSS 2400 ppm) had been uniformly mixed was obtained, 21 of an artificially adjusted solution containing 0.685 g/l of sodium sulfate and 0.01 g/l of potassium phosphate was added and circulated for two days such that the nitrogen-extracting bacteria were fixed. Next, a base water comprising a composition of the same artificially adjusted solution (nitrogen concentration 113ppm), and

methanol of 0.36ml per 10l of base water, were continuously passed through. On the other hand, for the sake of comparison, a case wherein nitrogen-extracting bacteria were caused to adhere to foamed bodies that did not have iron flock attached, and a case wherein the nitrogen-extracting bacteria were caused to adhere to active carbon were undertaken in parallel as well; the nitrogen-extraction rate results were such that, as shown in the following table, the method of the present invention exhibited the highest nitrogen-extraction rate.

EMBODIMENT 2

Similar to the first embodiment, 50ml of active sludge (pH 5.6) with MLSS of 2400ppm, and ferric chloride added such that it reached 500ppm, were added into a tower filled with ABS resin (diameter 5 m/m beads), and the full amount of nitrogen-extracting bacteria, which had been made into a flocked state, were injected such that they were caused to adhere to the resin.

Next, 2 liters of active sludge treatment water, that is petrochemical based wastewater, were added, and an adhered biological bed was formed by causing the liquid within the tower to circulate. 12ppm of $NO_2$- and 108ppm of $NO_3$- were contained in the active sludge treatment water, but because there was almost no presence of organic carbon, when a discharge water, prepared by adding an amount of methanol equivalent to 2.5 times the amount of nitrogen, was continuously passed through for two days, a nitrogen-

extraction rate of 97%, with a water-passage time of three weeks being equivalent to 60 minutes of contact, was obtained.

In comparison to prior art sludge contact circulation methods, the method of the present invention is superior from drive-management and placement area standpoints, and furthermore, because the support body is resin, which is extremely advantages from the standpoints of a lower cost as compared to the use of active carbon or the like, and the amount of material used, such that the present invention is also superior from a weight and handling standpoint.

Furthermore, the nitrogen-extraction rate is extremely high, and installation is compact; the removal of high concentrations of nitrogen is possible and the stability with regards to variations in water quality is high, such that the present invention can advantageously effect the removal of nitrogen from water.

[BRIEF DESCRIPTION OF THE DRAWINGS]

The figure shows a treatment tower as used in the embodiment.

1: Treatment tower; 2: Polystyrene foamed bodies; 3: Treatment water + Methanol; 4: Treated water

USPTO TRANSLATIONS BRANCH

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